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TRANSLATION INTO ENGLISH OF:

D2, Page 35, Third Complete Paragraph, Pages 40-48, 64-66

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The carbon enrichment to the level that is standard at the moment requires a minimum offer of H₂O in B₂O₃. An increase in the water content does not lead to a further C decrease. A carburization via the gas phase (CO, CO₂) evidently counteracts the process of C conversion in the GaAs. This is indirectly evidenced by the generation of C-poor pk GaAs reguli by means of gas change, wherein the balance setting was interfered with via the gas phase (see also item 5.3).

Pages 40-48

6. Monocrystal growth

6.1 Optimization of growing technologies with the system EKZ 900

The results shown in this section regard the studies carried out within the scope of the contract for growing GaAs monocrystals with an enhanced structural perfection and an improved reproducibility of the processes. After installation and putting into operation of the equipment and techniques taken over from WCT, the first task was to reach the yield and quality level of Wacker again. A subsequently performed analysis of the efficiency of the existing production methods showed signs of necessary optimizations within the scope of the given equipment variants. Emphasis was laid on the improvement of the 3" process, which was not satisfactory with respect to diameter

constancy and reproducible monocrystal growth. Extensive studies regarding the design of the furnace construction showed the limits of the low-pressure technique and led to a modification of the systems and to the development of a 3" technology at an increased inert gas pressure. Technical changes to the pulling systems led to a decrease in the number of total failures and to an altogether improved reproducibility of the growing process.

The goal to reach the Wacker level with respect to yield and dislocation density could already be achieved in the middle of the year 1992. Table 6.1.1 shows, by way of example, the mean values of the dislocation densities, calculated from the initial and final values of the test wafers for 2" to 4" crystal.

Crystal diameter	WCT (12/90) /1/	FEW (2/92) according to original WCT technology)	FEW (12/94) (opt. technology)
2"	42,000	46,000	40,000
3"	66,000	68,000	61,000
4"	80,000	75,000	72,000

Table 6.1.1: Comparison of the dislocation densities (EPD [cm⁻²]) of WCT and FEW (mean values on crystal beginning and end).

Optimizing operations carried out with respect to essential growing parameters, such as temperature control, position of the melt surface in the heater, or crucible lift rate, reduced the average dislocation density through a stabilization of the process. The level reached complies with the international standard and can only be lowered to a considerable extent by a fundamental modification of the LEC method or the use of various variants of the Bridgman method.

Investigations conducted for optimizing the 3" technology aimed at creating a reproducible monocrystal growth and at providing the prerequisites for an increase in the charge. First of all, an increase in the average monocrystal length of acceptable crystals by 45% could be achieved by analyzing the thermal conditions in the growing reactor and by adapting the growing parameters in the phase of the cone growth on the

whole. The reason for the frequently polycrystalline growth was found in an excessively strong thermal radiation of the crystal via the cylindrical surface. Apart from the axial temperature gradients required for the heat discharge via the crystal, excessively radial gradients were observed that led to non-linear components in the temperature field, thereby causing thermal stresses. When these thermal stresses exceeded a critical value (critical shear stress), which is small near the melting point of GaAs and thus rapidly reached, movement and multiplication of the dislocations are observed, resulting in small-angle grain boundaries and polycrystalline growth in the end. Thanks to the above-mentioned measure a rapid increase in diameter, based on the length of the crystal, was made possible, which restricted the crystal area with a good "visible contact" towards the cold vessel wall and the heat radiation resulting therefrom. The closeness to the "hot" heater after the set diameter had been reached subsequently prevented an undesired heat discharge in radial direction.

The shape of the crystallization front to be made visible by so-called "striation" etching is suited for controlling the heat flow into the vicinity of the phase boundary. The rule of thumb is: convexly shaped phase boundaries permit monocrystalline growth whereas concave / convex phase boundary shapes often lead to polycrystalline growth. The shape of the phase boundary was used as a yardstick for the assessment of changed assemblies used for growing.

The change in the cone growth in the case of the 3" growth did not constitute a basic solution of the problem. To permit a stable monocrystalline growth over the whole body length, crystals with a diameter above the diameter required for the production of 3" wafers had to be grown in the given furnace construction. This was accompanied by an unfavorable conversion of feed material into crystal length. The investigations described hereinafter were meant to solve this problem.

First of all, it was checked whether a growing near the set diameter could be achieved by changing the diameter ratio crystal : crucible / heater. At the same time, a more stable diameter control should be made possible through this method and the convexity

of the phase boundary should be improved. The first task has been fulfilled, but the convexity of the phase boundary deteriorated due to the melt level rising during use of crucibles with a smaller diameter at the same charge. The negative effect of an enhanced melt on the phase boundary convexity outweighed the advantage of the growing process on the set diameter from smaller crucibles and would have deteriorated the growth conditions further in the case of the intended increase in the charges. In addition, the greater closeness of the crystal to the heater caused a stronger decomposition of the surface of the crystals, necessitating unfavorably high crucible positions for the crystal growth. That is why this approach had been abandoned for the time being.

In further tests different heater lengths, changed post-heating systems and different graphite installations below the crucible were used. It was also found out here that improvements on the one hand were often accompanied by deteriorations of other growing parameters.

Although longer heaters permitted an easy increase in the charge, they led to an intensified radial heating of the crucible bottom at the same time in cases where it was not possible to carry out the growing process at an appropriate depth in the heater. The overheating of the crucible bottom deteriorated the convexity of the phase boundary. The deepest place that was possible for the phase boundary was limited on the other hand by the evaporation of arsenic from the near-surface regions. For these reasons the heater should only be as long as needed in installations having a single-heater system. This means long enough to prevent solidification of GaAs on the bottom and not too long to be able to perform growing near the temperature maximum of the heater without an excessive decomposition of the crystal part exiting from the boron oxide. This means also that at increased charges (and thus necessarily longer heaters) the growth conditions will deteriorate at any rate during the growing process.

To reduce the axial temperature gradient in the crystal and to limit the "visible contact" of the outer crystal surface towards the cold recipient wall, various passive post-heaters were tested. What was positive was a considerable reduction of the

temperature variations in the gas phase above the boron oxide to about 50% of the initial value. This would permit a more stable growing and better prevention of twin formations to a greater degree. This measure, however, was also confined by the problem of arsenic evaporation. Changes in the furnace constructions below the crucible allowed for a different heat discharge via the crucible bottom and thus a targeted variation of the convexity of the phase boundary.

The tests performed yielded a number of positive approaches for improving the growth conditions and for increasing the charges. In the final analysis these could not be realized or only realized to a limited degree because of the excessive decomposition of the crystal surface. In accordance with the finding that all efforts for growing long crystals with the low-pressure method are abortive without restriction or prevention of the formation of Ga channels, even if other essential growing parameters are mastered, the following investigations were primarily concerned with measures for reducing arsenic loss from the crystal surface and with the accompanying formation of Ga channels.

The change in the furnace structures for eliminating said problem aimed at

- a better protection of the crystal from the heater radiation,
- a better convective cooling of the crystal and
- the provision of an additional arsenic vapor pressure source.

The following measures were taken:

- the cooling surface for the inert gas was increased,
- the post-heater was modified,
- additional heat shields were mounted between crystal and heater,
- various crucible support plates and heaters of different length were tested,
- and an As vapor pressure source was installed.

On the whole, various growing assemblies were obtained for growing monocrystals within the present length range after optimization of other growing parameters. The main problem, i.e. considerable reduction of the arsenic evaporation, was however

not solved by these measures (see Fig. 6.1.1.), or it was only solved by accepting a deterioration of other growing parameters to an extent no longer allowing a stable monocrystal growth. It has been found that apart from the lateral heater radiation the thermal coupling between crystal and melt was so great that changes in the furnace structures in the surroundings of the crystal were no longer adequate as such. As expected, the use of argon instead of nitrogen as an inert gas showed no decrease in the loss of arsenic due to the heating capacity that was only half as high. The evaporation, which is more uniform with respect to nitrogen, over the circumference (several weaker Ga channels) alone does not represent a solution.

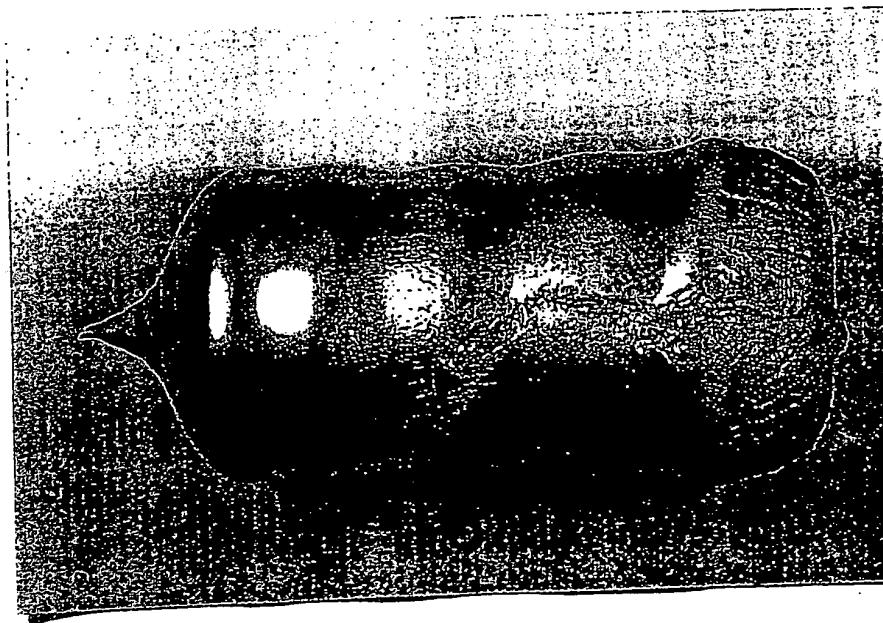


Fig. 6.1.1: 3" crystal no. 40668, produced according to the low-pressure method

On the whole, the charges could not be increased with the existing plant technology exploiting the low-pressure technique. However, the studies made as well as optimizations of the process parameters led to an essential stabilization of the 3" process with continuously improved yields. For instance, measures for lowering thermally caused stresses contributed to a significant reduction of crack formations, above all in the processing of Te-doped crystals. Plastic deformations of the crystals

could be reduced by decreasing the axial and radial temperature gradients during the cooling phase. Fig. 6.1.2 shows the development of the yield from 1992 till the end of 1994. The yield could almost be doubled during the report period as compared to the start level 1992 (= yield level at WCT in 1990).

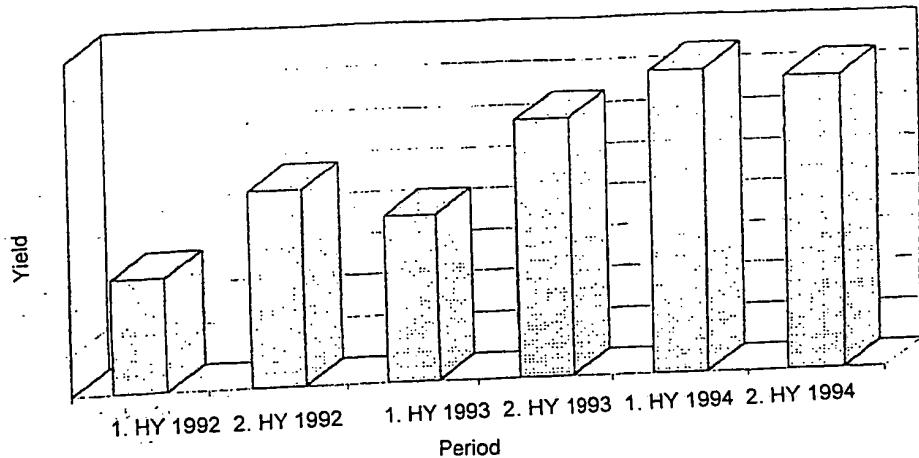


Fig. 6.1.2: Averaged yield development for 3" SI-GaAs monocrystals from 1992 to 1994

For eliminating the problem of arsenic evaporation from the GaAs source, a modified low-pressure facility was put into operation. This facility permitted the use of an increased inert gas pressure up to 10 bar. It was the aim to confine arsenic evaporation by an improved convective cooling of the crystal surface already at the initial stage. The first crystals grown with this system already showed that the method that had been adopted was correct. Using the standard charges, crystals with a high

structural perfection and **without** Ga channels could be grown. Fig. 4.1.3 shows a 3" crystal from an initial charge increased by 25%. The growing of crystals from initial quantities that had been increased by 40% could be carried out with success. For maintaining the monocrystalline growth over the crystal length, it was however necessary at the increased inert gas pressure to grow with a diameter above the diameter required for producing 3" wafers. That is why the tests that had been stopped in the low-pressure technique were once again resumed with respect to furnace structure with a greater ratio of crystal : crucible / heater diameter.

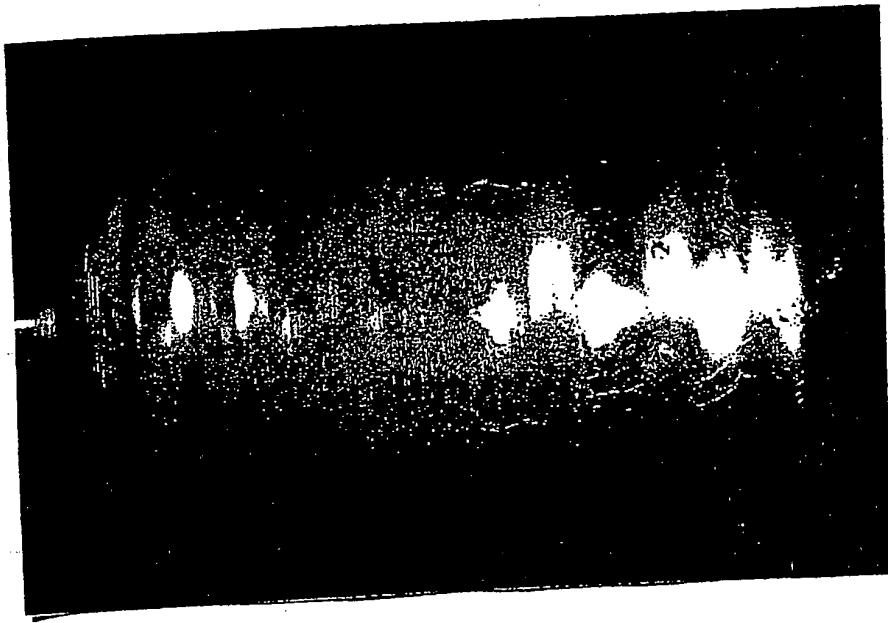


Fig. 6.1.3: 3" crystal no. 40644, produced according to the modified low-pressure method

Using an increased inert gas pressure, it was not possible to adopt the furnace structures from the low-pressure technique in an unrestricted way. An enhanced convection in the gas chamber of the recipient led to greater temperature variations in the surroundings of the phase boundary. Rapid increases in the diameter and re-

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melting processes during pulling of the seed extension and in the cone area augmented the probability of twin formation and polycrystalline growth. An adaptation of

- the resistance heater,
- the shield cover,
- and of the passive post-heater

to these conditions solved those problems. A further consequence of the increased gas convection was a stronger cooling of the crucible bottom. During crystallization it had the result that GaAs also solidified on the crucible bottom. The growing together of the crystal with the melt that had solidified on the bottom ended with the decline of the crystal. A useless crystal and a higher probability that the expensive pBN crucible would be destroyed upon removal of the material were the consequences. The problem could be eliminated by a new construction of the support plate.

The stronger convective cooling of the crystal surface permitted, without excessive crystal decomposition, a shifting of the position of the phase boundary between crystal and GaAs melt towards the temperature maximum of the heater to such an extent that a stable monocrystalline growth became possible.

After optimization of further growth parameters a technique could be developed that yielded reproducibly good results. In comparison with the low-pressure technique, the yield could be enhanced once again. In addition the improved conversion of the charge into crystal length led to an increase in the number of wafers per crystal by about 20%.

Apart from the technological developments, technical changes in the pulling facilities and improvements of the software led to a decrease in the number of total failures and to an altogether improved reproducibility of the growing process.

The uncontrolled change in the pulling speed was suppressed in the 2" and 3" process by modifying the pulling assembly. The equipment of the systems with "thunderstorm protection means" prevented emergency shutdown in case of short

power failures. Uncontrolled rotational changes by interference pulses were greatly reduced by software. Also introduced was a lifting of the crucible, which depended on the crystal diameter, for ensuring a constant melt surface position in the heater. Stable thermal conditions during the test are needed for making the growing processes reproducible, but also between different runs. A controlled convection of the inert gas is needed therefor. The measurement of the heater temperature used for controlling the process must yield stable values. Fig. 6.1.4 shows with reference to the example of the dip temperature that this was not always the case in the past.

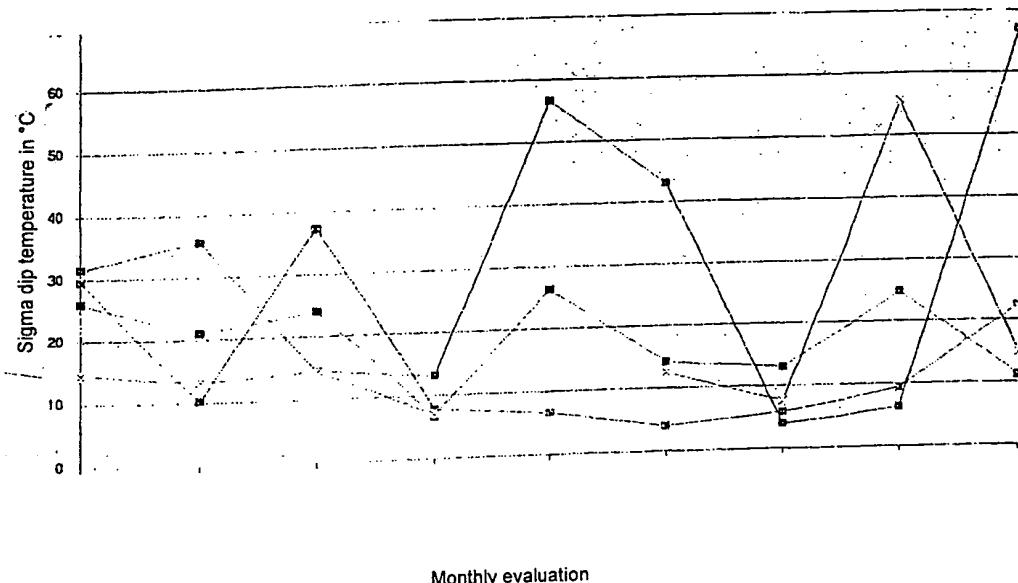


Fig. 6.1.4 Variation of the dip temperature in different low-pressure systems, each data point represents the variation within a month

Strong variations made above all the melting and nucleating process difficult. The reason was the reduced space available between the heater and the graphite shield for positioning the thermocouple. When the tip of the thermocouple was not exactly at the same place from test to test, considerable differences in the measured

temperatures could occur because of the large radial temperature gradient towards the cold vessel wall. A removal of the thermocouples after every test for cleaning the facility is unavoidable, so that another solution for this problem had to be found. The construction of the thermocouple mounting was revised and admissible variations in the dimensions were specified with the producer of the thermocouple. Since the temperature conditions were also influenced by the gas flow between heater and shield, an additional furnace component was tested with success, the component making said convection reproducible. Fig. 6.1.5 shows the sigma values of the dip temperature variation after said measures had been taken. Deviations from normally $>> 20^{\circ}\text{C}$ pose no problems and represent a considerable improvement over the previously arising variations up to 50°C .

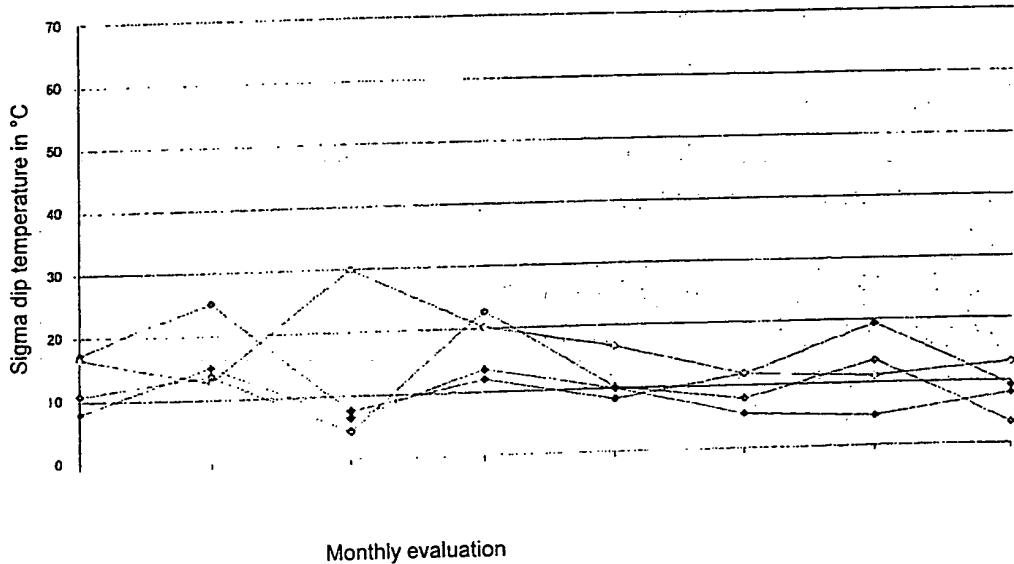


Fig. 6.1.5: Variation of the dip temperature of different low-pressure systems after realization of the measures; each data point represents the variation within a month.

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6.2.4.2 Solid doping with carbon

Two groups of problems had to be dealt with in connection with the direct doping of the GaAs with carbon. On the one hand, some kind of possibility had to be created for providing carbon amounts in the microgram range in a reliable manner (only 0.000004 g carbon is needed for providing 1 kg GaAs with 1×10^{15} at/cm³ C.). On the other hand the doped carbon had to be prevented from getting lost because of its low density before being dissolved in the melted GaAs. The first problem was solved in a satisfactory way. Carbon amounts in the order of 10 µg could be provided. Doping concentrations starting from 1×10^{15} at/cm³ onwards are adjustable. At an initial concentration of the melted gallium arsenide of less than 10^{14} at/cm³, the whole range of interest has thus to be covered. Test experiments showed that the method functions in principle and can be used both in the low-pressure and in the high-pressure range. Crystal material with a resistance up to 10^9 Ωcm was prepared. The carbon content was here up to 1.5×10^{16} at/cm³. As a rule, the C concentration measured in the crystal was clearly below the value to be expected from the addition. A considerable part of the carbon was thus bound to get lost at the beginning of the process.

For determining the mode of operation of the doping process, i.e., clarifying the question whether the carbon added is dissolved rapidly enough in the GaAs melt or whether it floats and reacts with the water of the boron oxide, thereby forming carbon monoxide, a crystal was grown by adding the carbon isotope ¹³ C. The natural isotopic abundance of the ¹³ C is only 1.1%, so that in an undoped crystal with a total carbon content of 1×10^{15} at/cm³ the concentration of ¹³ C is only at about 1×10^{13} at/cm³. Thus, a higher concentration is clearly due to doping. On the whole, with a

doping of the melt at about 5×10^{15} At /cm³ ¹³C on only one sample, a value above the detection limit of 2×10^{14} At / cm³ could be measured (Table 6.2.4.2.1).

Wafer	K1	K4	K5	E1
Axial position [mm]	27.0	65.9	100.7	154.2
¹² C [cm ⁻³]	1.47×10^{15}	1.11×10^{15}	1.08×10^{15}	9.7×10^{14}
¹³ C [cm ⁻³]	nn < 2×10^{14}	nn < 2×10^{14}	nn < 2×10^{14}	2×10^{14}
sum C [cm ⁻³]	1.47×10^{15}	1.11×10^{15}	1.08×10^{15}	1.21×10^{15}

Table 6.2.4.2.1: Carbon concentrations of the crystal 41260

The doped carbon was thus removed almost entirely at the beginning of the growing process. The result is surprising, but quite understandable if one only thinks of the amount of the available water in the boron oxide. The decrease in oxygen potential in the boron oxide, which accompanies the oxidation of carbon, permits in comparison with a growing without any C addition a recarburation of the GaAs over CO from the gas phase, which is then faster, so that the desired effect of an increase in resistance is efficiently achieved. For improving the reproducibility further tests are needed as to the most advantageous way of addition.

6.3 Technological development 3" with system type LPA3

Within the report period high-pressure systems of type LPA3 were again put into operation with the aim to exploit the variable technical and technological possibilities, and various techniques were developed for producing 3" crystals. The parallel production of low-pressure and high-pressure GaAs enabled our sector to conduct tests as to differences with respect to structure, chemical composition and physical properties. They led to a better understanding of the influence of various process parameters on the growth result and covered possibilities of selectively influencing the electrical properties of the material.

The technical start of the systems took place without any major problems. All of the system components showed a stable operation and the necessary precision. First of all the development of a 3" high-pressure technology for producing SI-GaAs from pBN crucibles was started. The necessary rule factors for an automatic diameter control were determined and further growing parameters were optimized. We succeeded in producing fully monocrystalline-grown crystals from charge sizes by analogy with the EKZ 800 technology. The extremely good diameter constancy of the crystals with variations of only a few millimeters ensured an optimum conversion of the charge into crystal length, contributing to a high material exploitation. An increase in the charge by around 12% was possible after modification of the furnace structure. With the change in the heater geometry and an improved heat insulation of the crucible bottom, crystal losses which had previously occurred at the end of the process of growing could efficiently be prevented.

Problems arose at the beginning of the development work with the homogeneity of the electrical properties (specific electrical resistance, Hall mobility). In axial direction there were changes in resistance in the order of 2 or 3, which was equal to the loss of the semi-insulating state towards the crystal end. An increased supply of oxygen due to the reaction of nitrogen with boron oxide to boron nitride according to the equation



was supposed to be the reason. After elimination of the oxygen source, we succeeded in keeping the specific electrical resistance over the whole crystal length above $1E7 \Omega \times cm$. With a change of < 8% over the wafer cross-section the high level of the low-pressure technique was almost reached in this field. Figs. 6.3.1 and 6.3.2 show a comparison of the crystals 250101 and 25031, which illustrates the elevated quality level in the course of the development. The axial curve and, by way of example, the radial curve of the specific electrical resistance are shown.